Understanding Performance Limitations in Thick Electrodes

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Project ID # bat363

Overview

Timeline

- Project start date: Oct. 2016
- Project end date: Sept. 2021
- Percent complete: 30%

Budget

- Total project funding
  - DOE share $ 50 M
- Funding for FY 2017: $ 10 M
- Funding for FY 2018: $ 10 M

Barriers

- Barriers addressed
  - **Performance**: need thick electrodes to reduce amount of inactive materials and to enable a 500 Wh/kg and 1000 cycle cell.

Partners

- PNNL: Battery500 lead, Jun Liu; Jie Xiao, cathode benchmarking
- BNL: Peter Khalifah, in-situ characterization
- Binghamton University: Stan Whittingham, cathode benchmarking
- University of Washington: Venkat Subramanian, modeling
- UT-Austin: Cathode materials

Relevance for Addressing Barriers

Overall objectives:

– Maximize the loading of the cathode material while maintaining capacity at C/3 to enable the Battery500 cell design

Objectives this period:

– Establish baseline performance for NMC811 material and enable the 350 Wh/kg cell design

Impact:

– Increasing electrode thickness reduces the number of layers and the amount of inactive materials, thus raising energy density and reducing cost

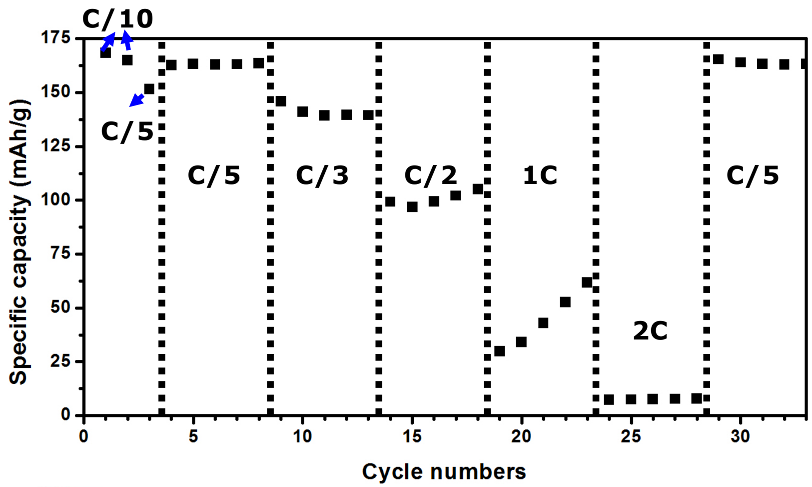
Keystone Project 2 Milestones for Electrode Architectures

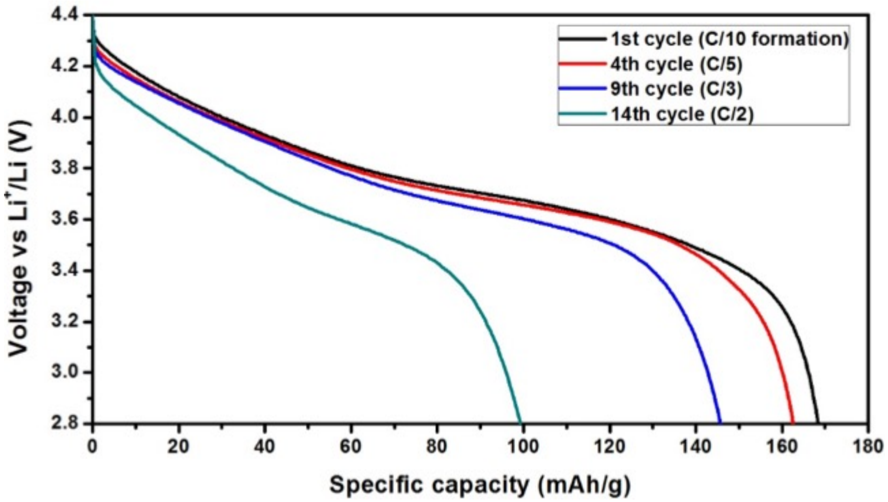
Milestones	Date	Status
1) Determine the optimized parameters of high-Ni NMC and S cathodes for Li metal pouch cells with >350 wh/kg energy density.	12/31/2017	Completed (Jie Xiao, **bat 369**)
2) Establish baseline cell performances of Li||high-Ni NMC and Li||S couples using stage II coin cell testing.	3/31/2018	Completed (Jie Xiao/Eric Dufek, **bat 368**)
3) Evaluate new concepts in stage II baseline coin cells, including new electrolytes, cathode surface modification, new polymer membrane, and Li metal anodes.	6/30/2018	On track
4) Provide feedback to Keystone project 1 team on how to refine these concepts for better performances	9/30/2018	On track

Approach

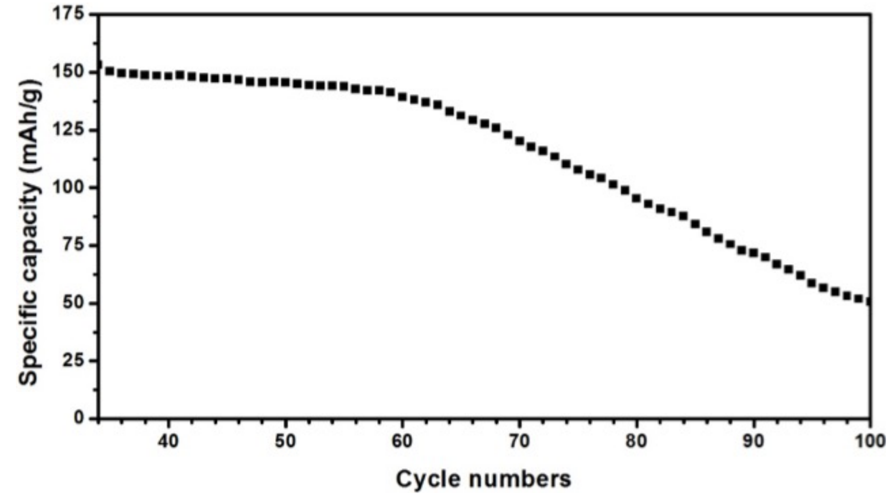
- Evaluate thick electrodes supplied by partner (Maxwell)
- Establish performance baseline for NMC622 and 811 sourced from different partners and vendors
- Optimize electrode fabrication composition and process
- Study the effect of electronic and ionic resistance on electrode performance

Dry-Method Thick Electrode Characterization





Cycling performance (at C/3)

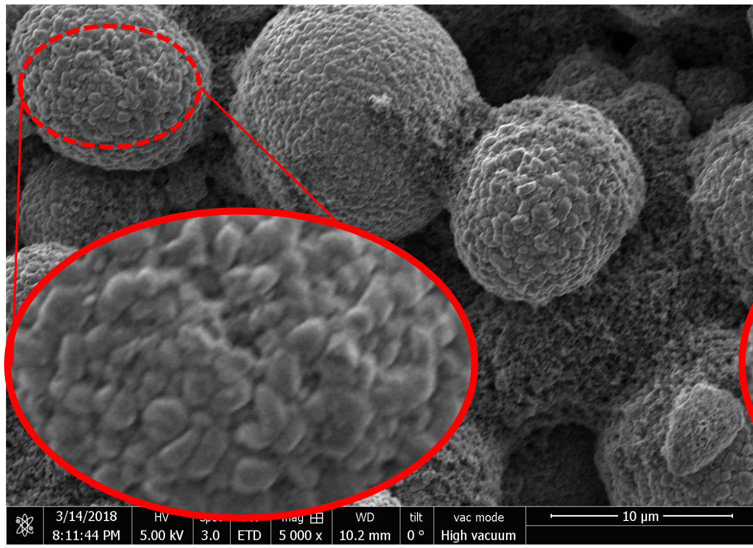


Maxwell dry method for electrode fabrication, 30 mg/cm^2, NMC622, active 94 wt%

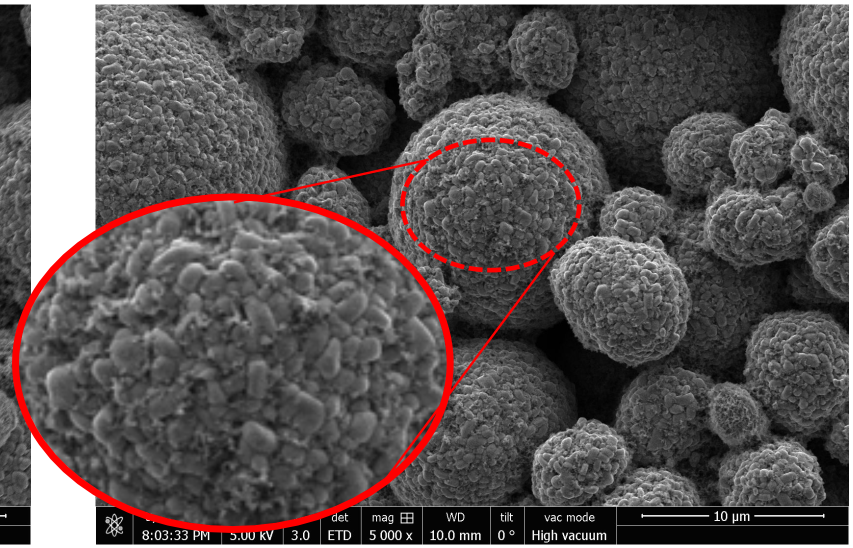
Electrodes have high loading and stable cycling until lithium failure

Optimizing NMC 811 Electrode Performance: Effect of Binder

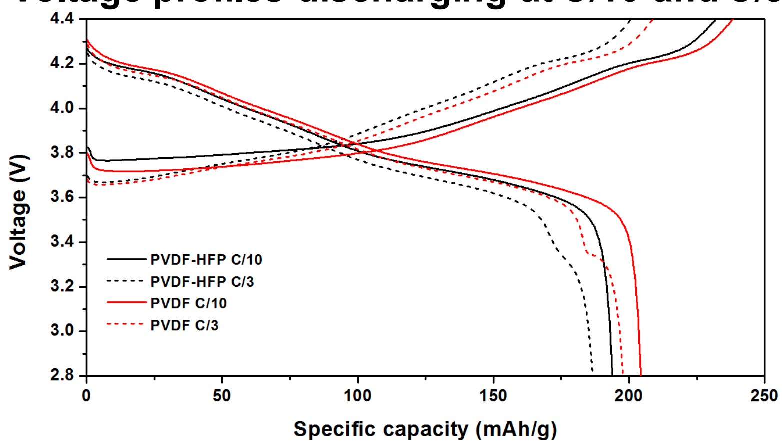
PVDF-HFP



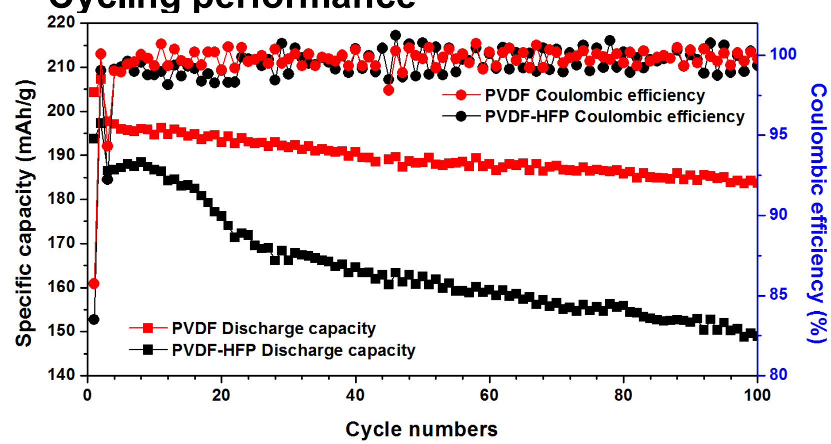
PVDF



Voltage profiles discharging at C/10 and C/3



Cycling performance



96 wt% active, 20 mg/cm^2

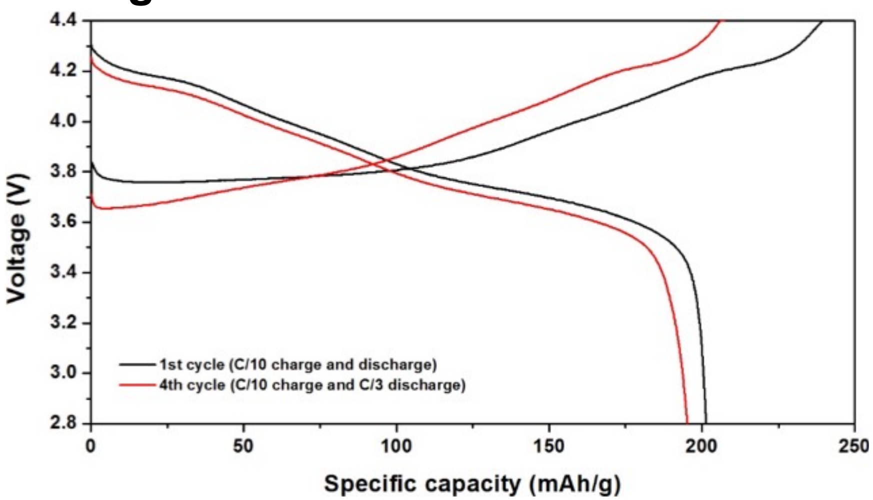
In collaboration with PNNL

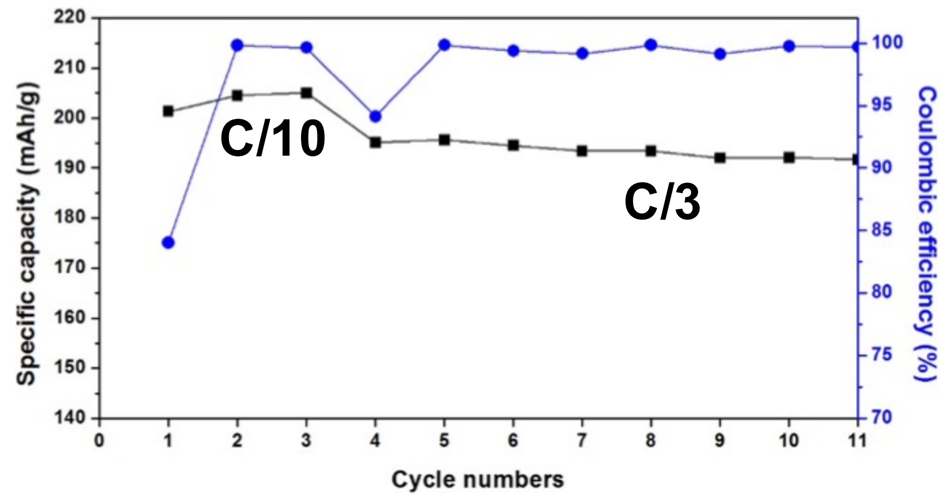
Binder choice is critical for homogeneity and electrochemical performance

BATTERY 500 CONSORTIUM

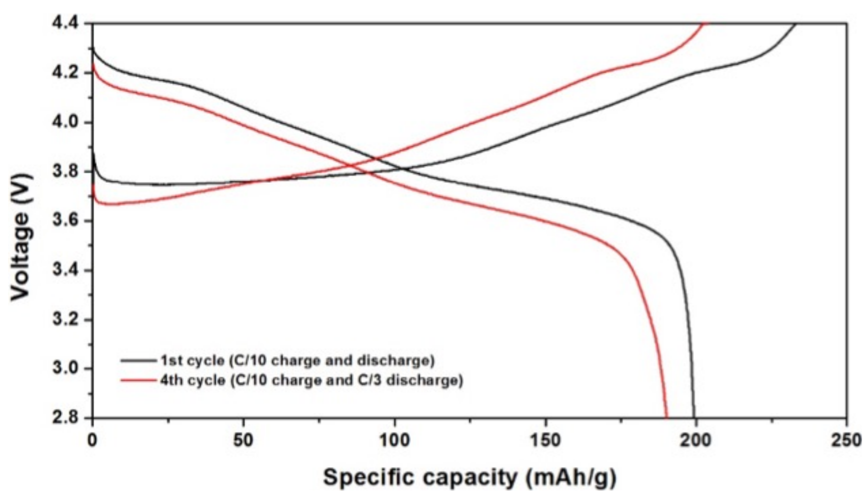
Effect of Raising Electrode Loading

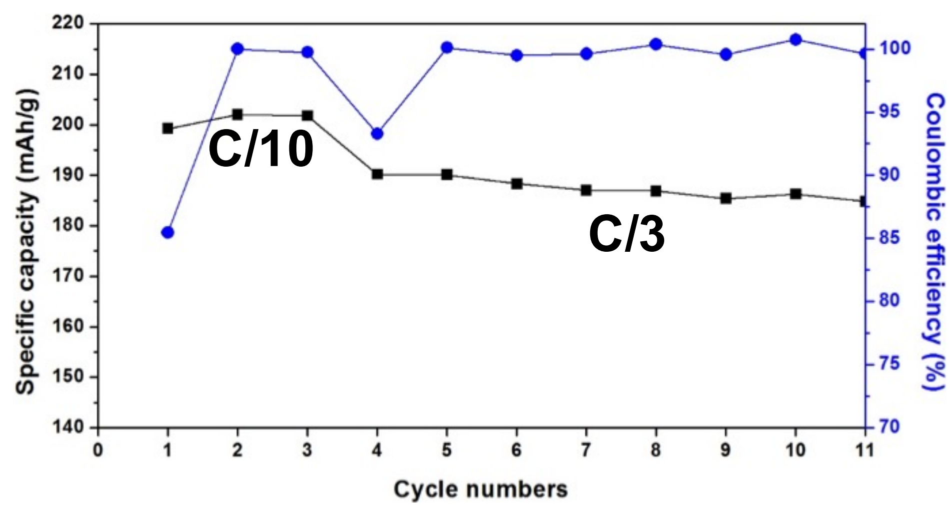
19 mg/cm^2





30 mg/cm^2



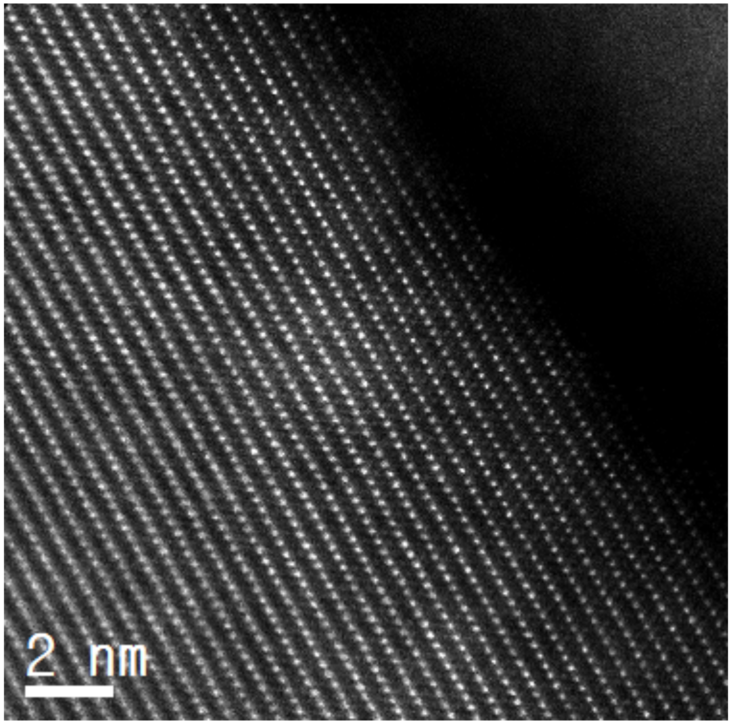


High areal capacity (5.7 mAh/cm^2) at 30 mg/cm^2 loading is possible

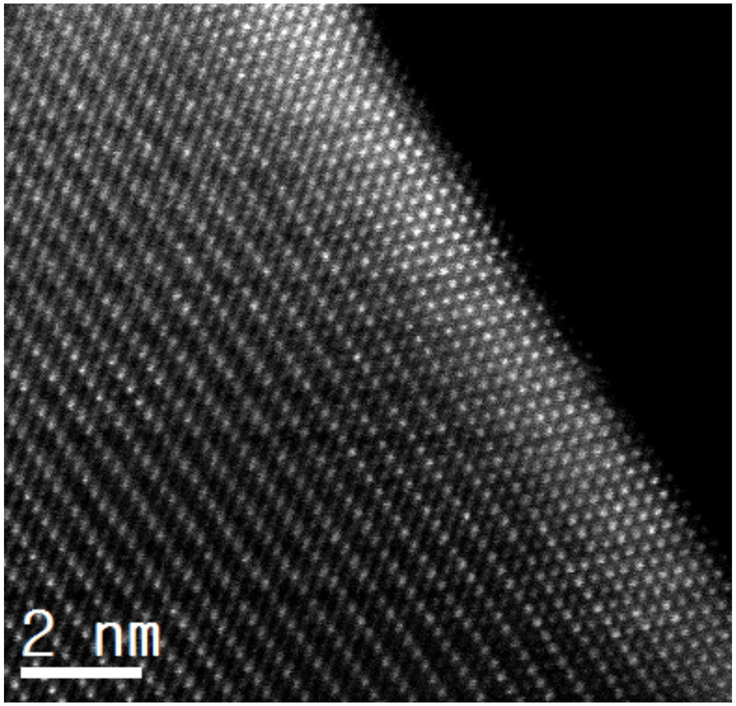
Understanding NMC811 Structure Stability

- High resolution images of commercial NMC811 show that only surface structure goes through reconstruction while bulk structure remains robust even after long cycling high-voltage cutoff (2.5-4.7V).

Pristine NMC811

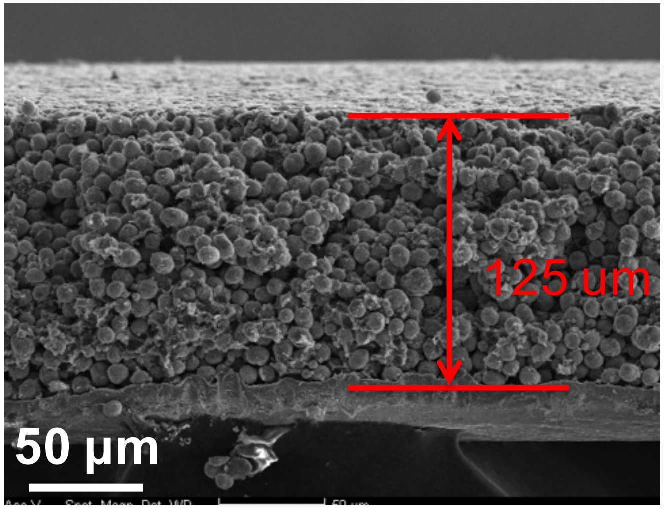


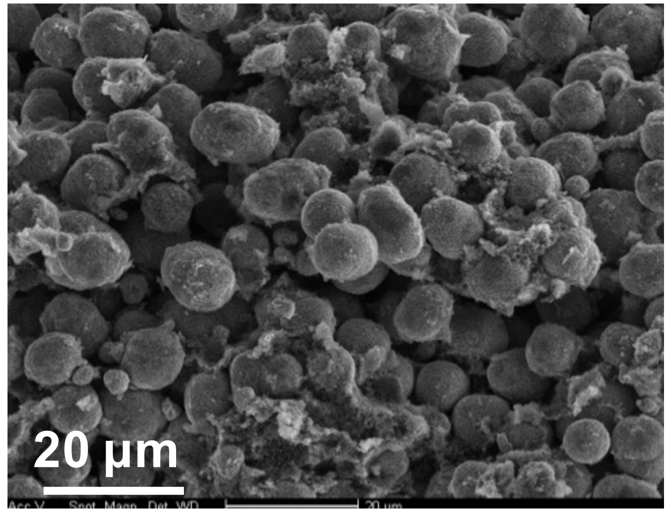
60-cycled NMC811



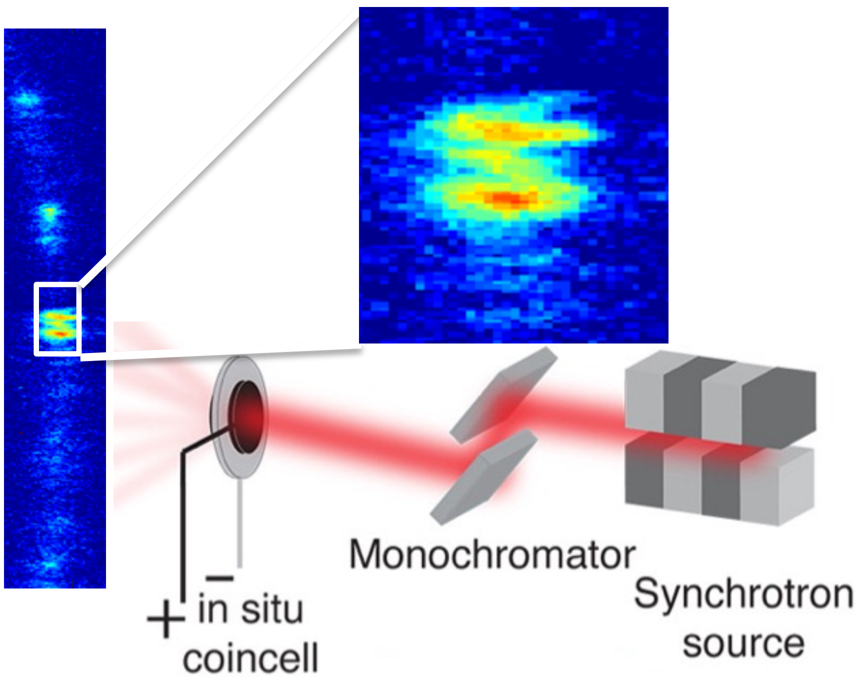
NMC811 has exceptional structural stability

Understanding Thick Electrode Inhomogeneity

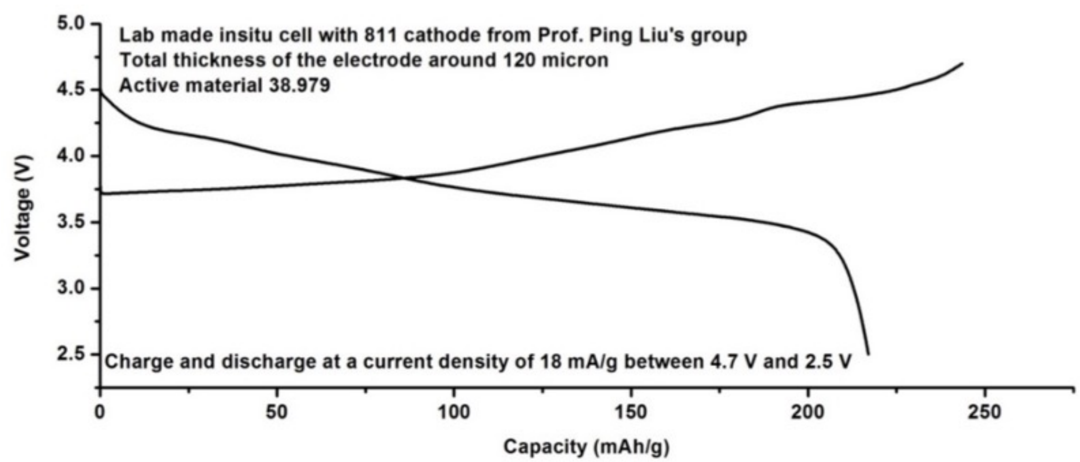




- 90% active materials
- ~30 mg/cm^2
- ~130 um
- 40% porosity



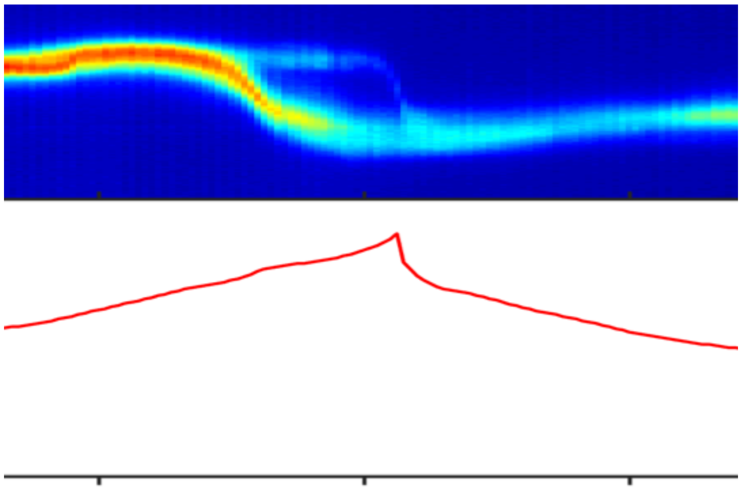
Experimental setup and Debye Scherrer pattern example



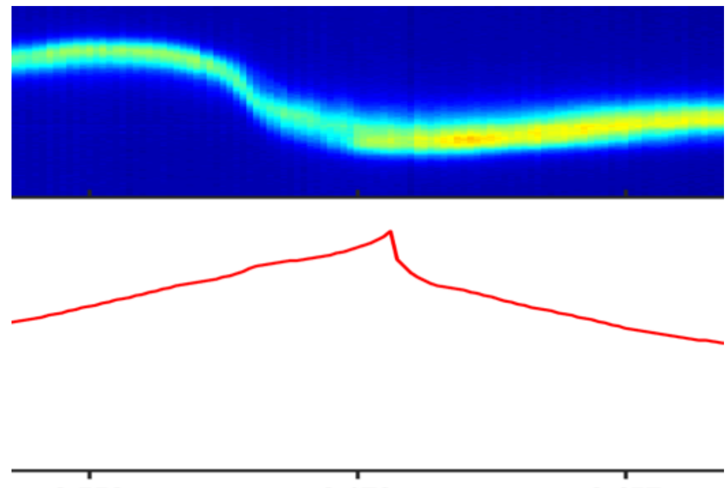
The battery was monitored by operando coherent X-ray diffraction imaging (CXDI) at C/10 rate for 1 cycle.

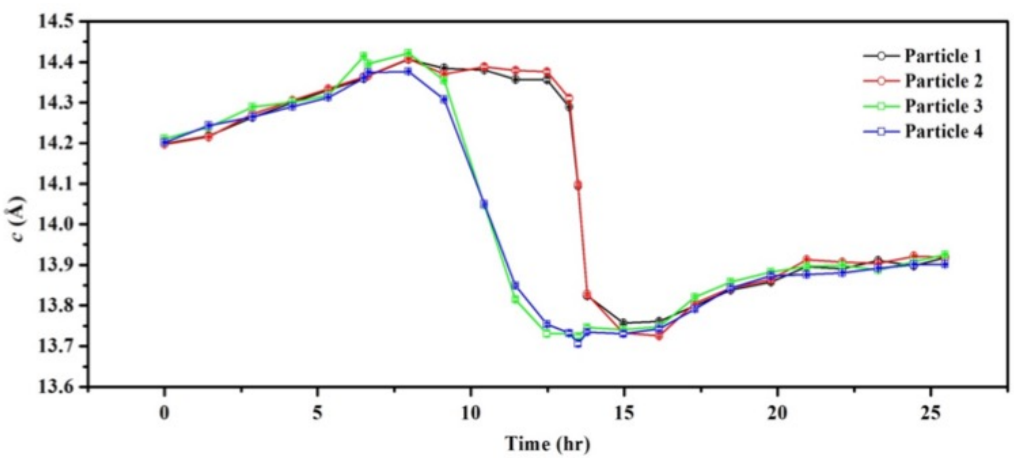
Observing Thick Electrode Inhomogeneity

C/10 position 1 beam exposure 30s



C/10 position 2 beam exposure 30s





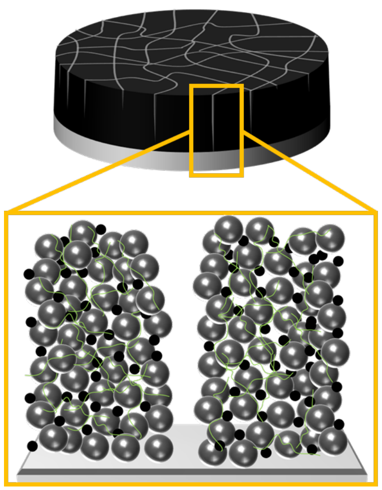
Single Particle Region
at C/10 position 1 beam exposure 30s

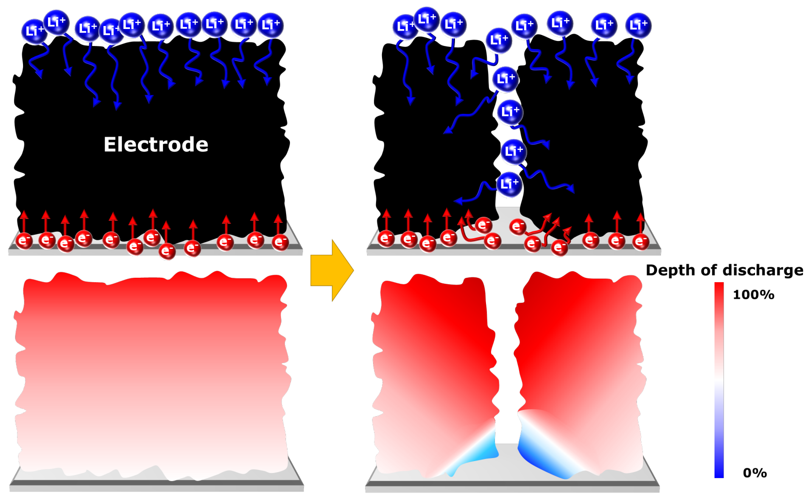
- A sluggish change of c-lattice parameter for some particles is identified at Position 1; all the particles transform more or less simultaneously at Position 2.
- Under-utilization of electrodes is also characterized using depth profiling, see **Bat367**

Inhomogeneity observed in thick electrodes

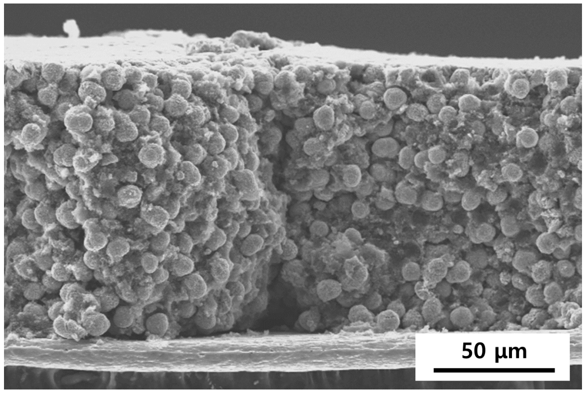
Microstructure Control to Understand Performance Limitations of Thick Electrodes

- Mud crack intentionally to create straight, vertical channels to reduce ionic resistance


Mud-crack formed electrode

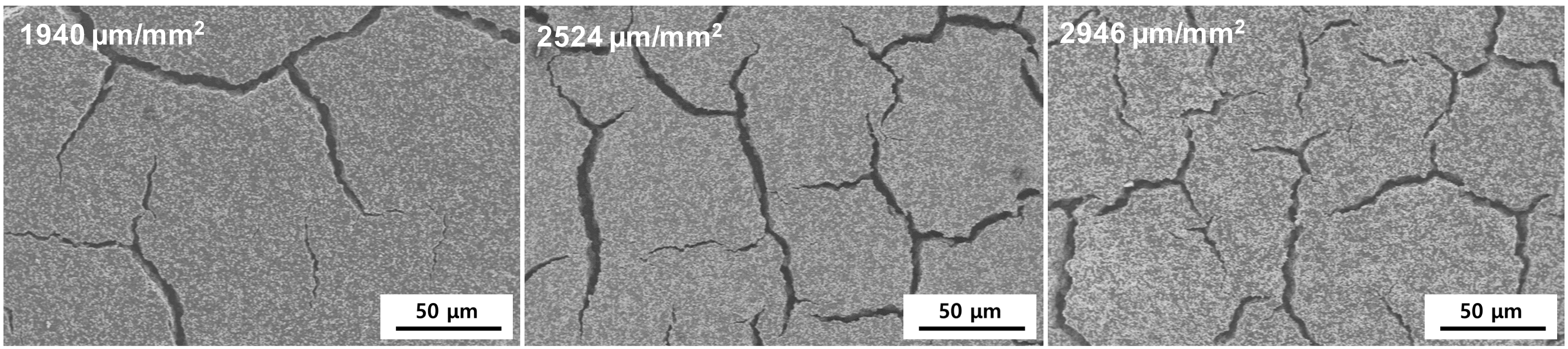


Expected depth of discharge profile



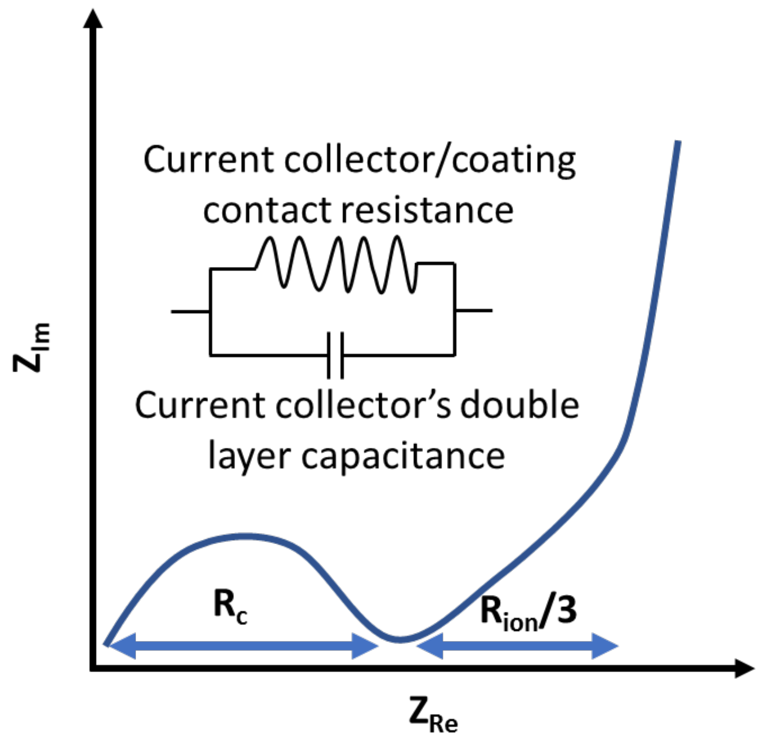
Calendared electrode with hairline crack

- Crack density control



Deconvoluting Electronic and Ionic Resistances

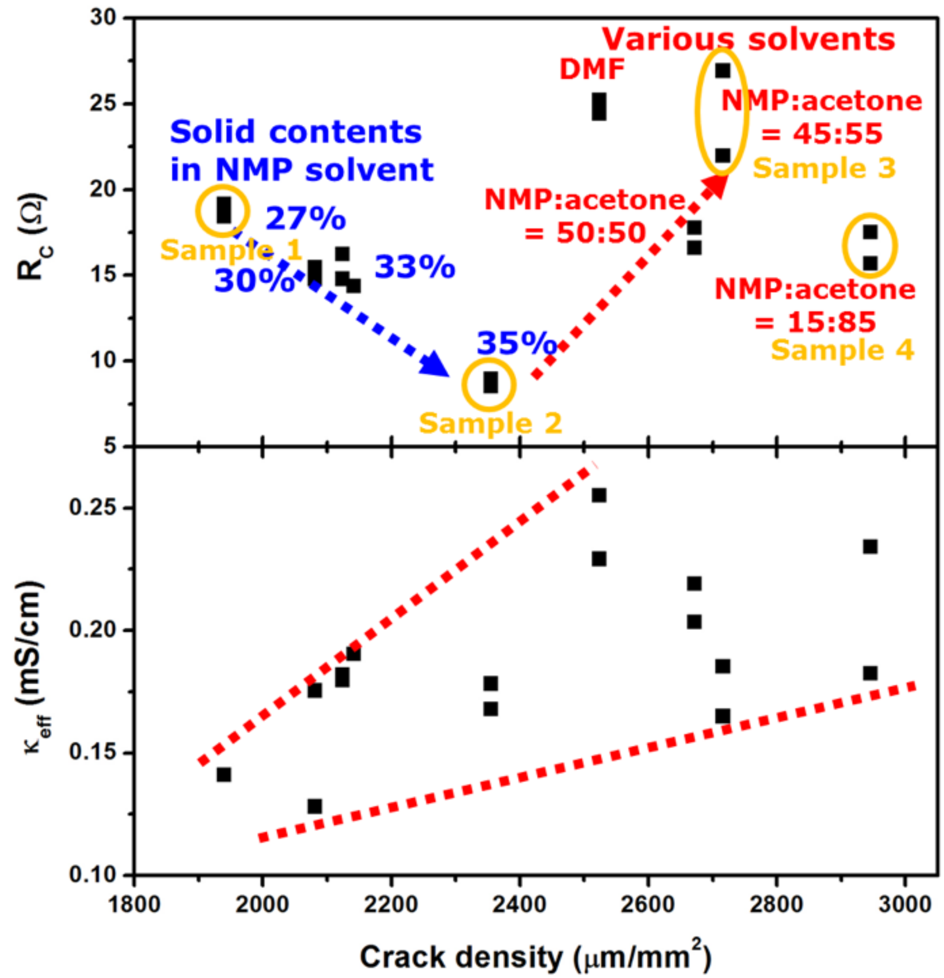
Schematic EIS curve for a symmetric cell with on-intercalating electrolytes



- R_c: Current collector – coating contact resistance
- R_{Ion}: ionic resistance → used for calculating ionic conductivity (κ_{eff})

Landesfeind, et al, J. Electrochem. Soc., 163 (7) A1373 (2016)

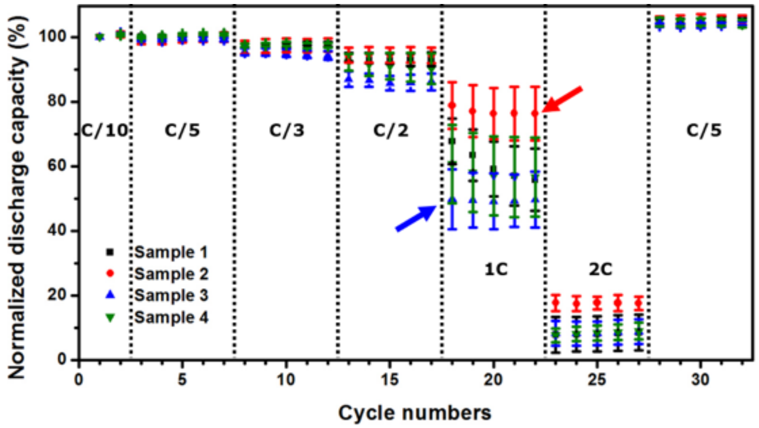
Contact resistance and ionic conductivity



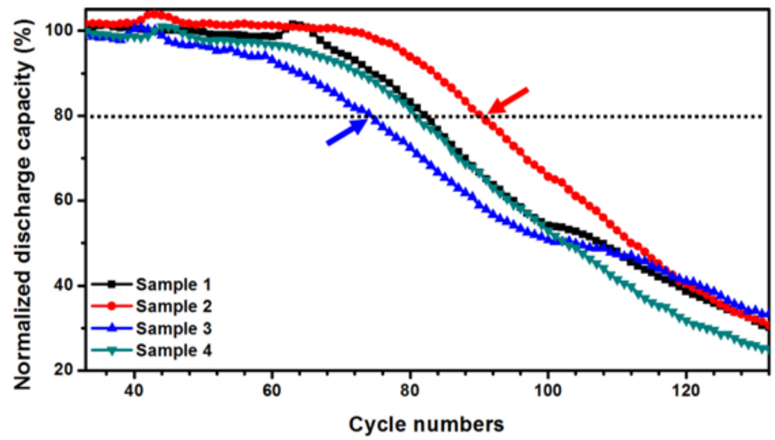
Electrodes created with same composition and porosity but different tortuosity and resistance

Correlating Impedance with Electrode Performance

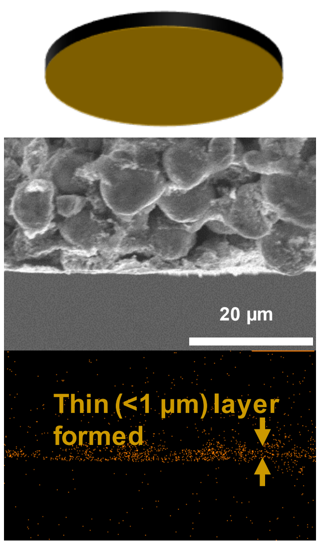
Rate performance



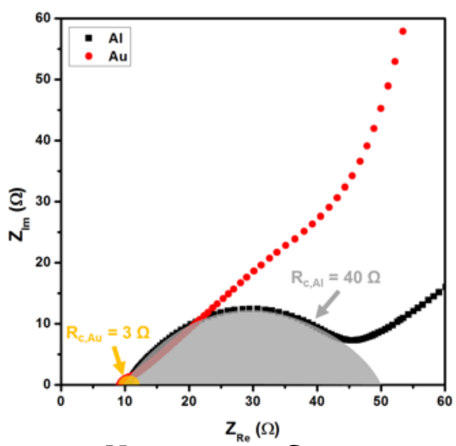
Cycling performance (at C/3)



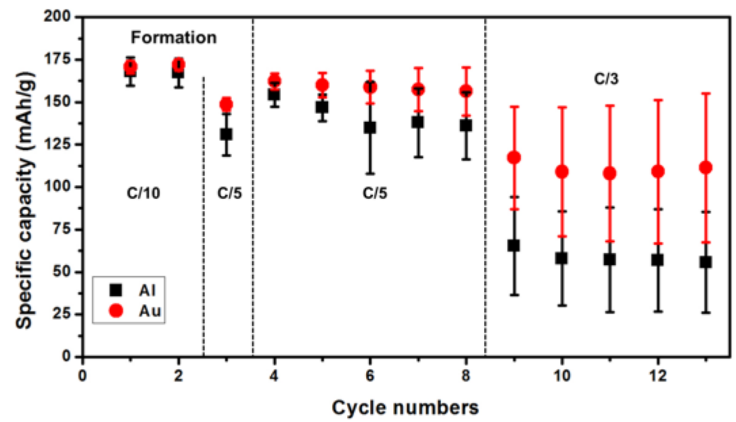
Further examination of interfacial contact effect with Au coated electrode



EIS of symmetric cells



Rate performance



- Both rate and cycling performances are intimately related to contact resistance
- Further work needed to reduce tortuosity without raising contact resistance

Responses to Previous Year Reviewers' Comments

- New project

Partners and Collaborators

- Brookhaven National Laboratory: in-situ XRD to understand state of charge distribution along the thickness of the electrodes
- University of Washington: electrochemical modeling of advanced electrode architectures
- Pacific Northwest National Laboratory: NMC811 materials and electrodes to bench mark electrode fabrication and testing
- Binghamton University: NMC811 data exchange
- UT-Austin: synthesis of NMC811 materials

Remaining Challenges

- Develop approaches to reduce tortuosity without raising electronic resistance;
- Demonstrate long term cycling stability without the interference from the lithium counter electrode;
- Quantitatively understand contributions of electronic and ionic contributions to electrode polarization for very thick electrodes.

Proposed Future Research

- Correlate electrode homogeneity with performance by integrating electrochemical and in situ depth profile SOC measurement;

- Develop approaches to enhance electronic conductivity with minimal use of binder and carbon;

- Use cathode/cathode symmetric cells to measure cycling and rate performance.

Summary

- Baseline NMC811 has shown stable cycling for 100 cycles with > 190 mAh/g capacity at 20 mg/cm^2 loading, sufficient for 350 Wh/kg cell design;

- Binder choice is critical for electrochemical performance;

- Crack formation was used to reduce tortuosity but at the expense of electronic conductivity;

- Next step will focus on developing methods to realize low tortuosity and high conductivity simultaneously.